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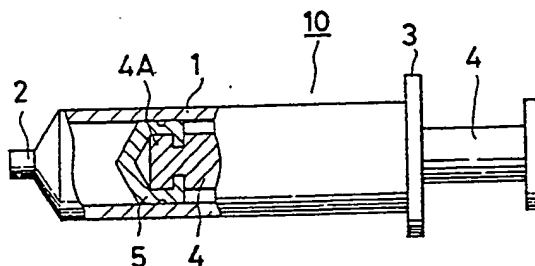
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54 Gasket and medical device using the same.

57 A gasket is made of a composite comprising hydrogen-added derivative (component a) of styrene-butadiene block copolymer, plasticizer (component b), and a polyethylene resin having a density of 0.940g/cm<sup>3</sup> or more (component c).

A medical device includes a cylindrical body and a gasket capable of moving in closely contact with the inner surface of the cylindrical body. And the gasket of the medical device is the same of the aforesaid type of the gasket.

FIG.1



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# GASKET AND MEDICAL DEVICE USING THE SAME

## BACKGROUND OF THE INVENTION

5 [Industrial Field of the Invention]

The present invention relates to a gasket and a medical device using the same.

10 [Prior Art]

There are medical devices such as disposable injectors each of which comprises a cylindrical body and a gasket which can move in closely contact with the inner surface of the cylindrical body.

15 Conventionally, the above-described gasket is made of, as disclosed in Japanese Patent Publication No. 59-18427(USP4303070), vulcanized rubber or styrene type thermoplastic elastomer (to be called "TPE" hereinafter). The styrene type TPE is made of a composite consisting of hydrogen-added derivative of styrene-butadiene block copolymer, plasticizer, and polypropylene for improving workability and for adjusting the hardness.

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[Problems to be Overcome by the Invention]

25 However, it needs a large facility to manufacture the gasket made of the vulcanized rubber since such a gasket is manufactured after it has been subjected to a complicated vulcanization process. Furthermore, a variety of additives such as sulfur, a vulcanization accelerator, and a filler are necessary. As a result, there is a fear of an elution of the additives into the liquid medicine when the medical device is used.

30 On the contrary, although the gasket made of the styrene TPE exhibits an advantage in the formability at the time of the injection molding and another advantage in that the fear of elution of sulfur can be eliminated, it is disadvantageous to vulcanized rubber in terms of the elasticity of the rubber, where the term "the elasticity of rubber" means in particular in the tensile characteristics that the inflection points such as the yielding points are reduced as possible and also the modulus (for example, the stress when expanded by 300%) is at a relatively high level in the relationship with the hardness. That is, in the styrene TPE, polypropylene which is the component of it causes the inflection point such as the yield point to be

35 generated and causes the modulus to be lowered in the tensile characteristics. Therefore, in a case where the gasket made of the styrene TPE is employed in an injector, the displacement added to a portion to be pushed does not immediately correspond to the distance of movement of the gasket. Therefore, a problem arises in that the gasket intermittently moves, that is, a so-called pulsation phenomenon takes place.

40 An object of the present invention is to provide a gasket and a medical device using the same, the gasket exhibiting an excellent formability and safety against elution and capable of preventing pulsation phenomenon.

## DISCLOSURE OF THE INVENTION

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A gasket in accordance with the present invention in claim 1 is made of a composite comprising hydrogen-added derivative (component a) of styrene-butadiene block copolymer, plasticizer (component b), and a polyethylene resin having a density of 0.940g/cm<sup>3</sup> or more (component c).

50 A gasket in accordance with the present invention in claim 2 is that the composite is formed by mixing 100 parts by weight of the component a and the component b with 10 to 50 parts by weight of the component c, the 100 parts being the total of the component a by 40 to 60 wt% and the component b by 60 to 40 wt%.

A gasket in accordance with the present invention in claim 3 is made of a composite comprising hydrogen-added derivative (component a) of styrene-butadiene block copolymer, softener for rubber

(component b), a polyethylene resin having a density of 0.940g/cm<sup>3</sup> or more (component c), and a hydrocarbon-type wax (component d).

A gasket in accordance with the present invention in claim 4 is that the composite is formed by mixing 100 parts by weight consisting of the component a and the component b with 10 to 50 parts by weight of the component c, and 2 to 20 parts by weight of the component d, the 100 parts being the total of the component a by 40 to 60 wt% and the component b by 60 to 40 wt%.

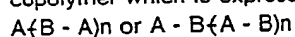
A medical device in accordance with the present invention in claim 5 comprises a cylindrical body and a gasket arranged in close contact with the inner surface of the cylindrical body and adapted to slide therein, the gasket being one obtained in accordance with any one of Claims 1 to 4.

#### [Operation]

The components and mixture proportion of the composite forming the gasket of this invention will now be described in detail.

#### Composite a

The above-described component a used in this invention is a hydrogen-added derivative of a copolymer which is expressed by the general formula:



[where A represents a polymer block of styrene, B represents a polymer block of butadiene, and n represents an integer ranged between 1 and 5].

In order to maintain the elastomer characteristics, it is desirable that the polymer block B employ a polymerization condition in which the proportion of the 1,2-micro structure in the micro structures in polybutadiene becomes 20 to 50%, and in particular, a polymerization condition in which the proportion of the 1,2-micro structure is 35 to 45%. Further, it is desirable that the proportion of the polymer block B in the above-mentioned copolymer be at least 65 wt%.

The number average molecular weight of the hydrogen-added block copolymer constituting the above component a is preferably in the range of 5,000 to 1,000,000, more preferably, in the range of 10,000 to 800,000, and still more preferably, in the range of 30,000 to 500,000. Its molecular weight distribution, that is, the ratio of its weight average molecular weight ( $\overline{M}_w$ ) to its number average molecular weight ( $\overline{M}_n$ ) : ( $\overline{M}_w / \overline{M}_n$ ) is 10 or less. Further, the molecular structure of the hydrogen-added block copolymer may be a straight-chain structure, a branch structure, or a radial structure, or an arbitrary combination of these structures.

These block copolymers may be manufactured by any manufacturing method as long as the above structure can be obtained. The hydrogen-added block copolymer used in this invention can be synthesized, for example, by first synthesizing a styrene-butadiene block copolymer in an inactive solvent using a lithium catalyst or the like in accordance with the method disclosed in Japanese Patent Publication No. 40-23798, and then adding hydrogen to the block copolymer thus obtained in an inactive solvent in the presence of a hydrogen-adding catalyst in accordance with the method disclosed in Japanese Patent Publication No. 42-8704, 43-6636, or the methods disclosed in Japanese Patent Laid-Opens No. 59-133203 and 60-79005.

It is preferable that the addition of hydrogen in the manufacturing process for the block copolymer for the component a of this invention is conducted such that hydrogen is added at least 50%, preferably 80% or more of the olefinic linkages in the polymer block B and hydrogen is also added to 25% or less of the aromatic unsaturated bonds in the polymer block A. As the block polymer of this type, a polymer on the market such as KRATON-G (the trade name of a polymer manufactured by Shell Chemical) can be used.

#### Component b

It is preferable that a mineral oil type or synthetic resin plasticizer is used as the component b which is the plasticizer according to the present invention.

The mineral type plasticizer is a mixture consisting of aromatic rings, naphthene rings, and paraffin chains. The plasticizer is classified such that the mixture in which the number of carbons in the paraffin chains exceeds 50% is called a paraffin type plasticizer, the mixture in which the same in the naphthene rings is ranged between 30 and 45% is called a naphthene type plasticizer, and the mixture in which the

number of the aromatic carbons exceeds 30% is called an aromatic type plasticizer. The preferable mineral type plasticizers as the component b of the present invention are the naphthene type plasticizer and the paraffin type plasticizer in which the proportion of the aromatic hydrocarbon thereof is less than 30%. The aromatic plasticizer is not preferably used in terms of dispersion characteristics with respect to the above-described component a according to the present invention.

The properties of the mineral type plasticizer are arranged such that the coefficient of kinetic viscosity at 37.8 °C is 20 to 500 cst, the pour point is -10 to -15 °C, and the flash point (COC) is 170 to 300 °C.

Although polybutene, low molecular weight polybutadiene, or the like can be used, the mineral type plasticizer is preferably used.

### Component C

The polyethylene resin of the above-mentioned component c is a high-density polyethylene resin with a density of 0.940g/cm<sup>3</sup> or more and can be obtained by the normal method (the low-pressure polymerization method). The MFR adopted is 0.1 to 50g/10min at 190 °C under a load of 2.16kgw.

Normally, in addition to a plasticizer, a resin component (e.g., polypropylene) is generally added to a thermoplastic elastomer based on styrene-butadiene copolymer with a view to adjusting its hardness and workability. This invention is characterized in that a certain amount of polyethylene resin is added as this resin component.

The melting point of a polypropylene resin (about 160 °C) is higher than that of a polyethylene resin (about 120 °C). Further, a polypropylene resin exhibits a higher modulus of flexural elasticity. Under the circumstances, it has been believed that a thermoplastic elastomer having a satisfactory heat resistance and rubber elasticity can be obtained by using a polypropylene resin. However, the inventors of this invention has found out that, by using, instead of a polypropylene resin, a polyethylene resin with a density of 0.940g/cm<sup>3</sup> or more, a substantial improvement in rubber elasticity and heat resistance can be attained. A polyethylene resin density of less than 0.940g/cm<sup>3</sup> results in excessive bleeding of the plasticizer and insufficient heat resistance (permanent compression strain).

### Component d

The hydrocarbon-type wax constituting the component d used in this invention for the purpose of improving the workability (fluidity and mold appearance) may be a paraffin wax obtained through petroleum refining and exhibiting a melting point of 40 to 100 °C and a 100 °C viscosity of 1 to 30 cSt or a polyethylene-type wax obtained through polymerization and exhibiting a dropping point (ASTM-D-3104) of 90 to 120 °C and a 140 °C viscosity (Brookfield) of 40 to 7,000cps. A hydrocarbon-type wax preferable as the component d of this invention may be a polyethylene-type wax.

### Mixture and Kneading

The mixture proportion of the components constituting the TPE (thermoplastic elastomer) of this invention may be such that the proportion of the component a with respect to the total amount of the component b is 40 to 60 wt%, preferably, 40 to 55 wt%. If the proportion is less than 40 wt%, the rubber elasticity and heat resistance of the TPE obtained will be rather poor, with the bleeding of the plasticizer being deteriorated. If it is more than 60 wt%, the flexibility, formability and workability of the TPE will be deteriorated. The proportion of the component b is to be 60 to 40 wt%, preferably, 60 to 45 wt%. If the proportion is more than 70 wt%, the rubber elasticity and heat resistance of the TPE will be rather poor, with the bleed-out of the plasticizer being deteriorated. If it is less than 40 wt%, the flexibility, formability and workability of the TPE will be deteriorated.

The proportion of the component c to 100 parts by weight of the sum total of the components a and b is to be 10 to 50 parts by weight, preferably, 10 to 30 parts by weight. If the proportion is less than 10 parts by weight, the formability and workability will be poor; if it is more than 50 parts by weight, the flexibility of the TPE will be lost, and, at the same time, the bleed-out of the plasticizer will deteriorate.

The proportion of the component d, which is used in this invention for the purpose of improving the workability (fluidity and mold appearance), is to be 2 to 20 parts by weight, preferably 3 to 10 parts by weight, with respect to 100 parts by weight of the sum total of the components a and b. If the proportion is

less than 2 parts by weight, the resulting mold appearance will be an unsatisfactory one; if it is more than 20 parts by weight, the flexibility and rubber elasticity of the TPE will deteriorate.

While the present invention is characterized in that these necessary components are contained by a certain quantity when obtaining TPE, an additional component such as a polyolefine polymer, a polystyrene polymer, or an inorganic filler may be added in a range which does not involve deterioration in the basic performance of the invention, the inorganic filler including calcium carbonate, talc, mica, and carbon black. Furthermore, in order to meet the aiming property, additives such as an antioxidant, ultraviolet absorber, slipping agent, and fluidity accelerator may be added.

The TPE according to the present invention can be manufactured by the mechanical melt kneading. Specifically, a usual mechanical melt kneader such as a Banbury mixer, various kneaders, single or two-shaft extruder can be used.

The TPE according to the present invention may be formed by the method of molding thermoplastic resin such as the injection molding, extrusion molding, and blow molding.

Thus, the TPE forming the gasket of this invention contains, instead of the polypropylene constituting the conventional styrene-type TPE described above, a polyethylene resin having a density of 0.940g/cm<sup>3</sup> or more, thereby making it possible to secure satisfactory formability and safety against elution without spoiling the rubber elasticity which is inherent in a hydrogen-added derivative of styrene-butadiene block copolymer. As a result, a gasket and a medical device using the same which exhibits an excellent formability and safety against elution without any problem of pulsation phenomenon can be obtained.

## BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a schematic view of an injector in which the gasket according to the present invention is used, and Fig. 2 is a diagram which illustrates the results of a pulsation test.

## BEST MODE FOR CARRYING OUT THE INVENTION

In an injector 10 shown in Fig.1, reference numeral 1 represents a syringe made of hard synthetic resin, 2 represents a nozzle, and 3 represents a flange. Reference numeral 4 represents a body to be pushed which is made of hard synthetic resin, and 5 represents a gasket according to the present invention which is fitted to a front portion 4A to be engaged of the body 4 to be pushed.

In the following embodiments and comparative examples, the testing methods for making various evaluation were as follows, where test sample was a 2mm-thickness sheet (sample for the following tests (1) to (3)) manufactured by a 5-ounce in-line screw type injection molding machine under the conditions that the injection pressure was 500 kgf/cm<sup>2</sup>, injection temperature was 220 °C, and the temperature of the mold was 40 °C. Furthermore, another test sample was a gasket for 5ml syringe having the peak diameter of 13.2mm (sample for the following tests (4) to (7)). The inner diameter of the outer cylinder for 5ml-syringe was 13.0mm.

### (1) JIS-A hardness \*\*\* JISK-6301

If the gasket for a cylinder is too hard, the sliding ability is insufficient and the assembling of it is difficult. On the contrary, if it is too soft, it cannot be strongly engaged to the body to be pushed, causing the separation of them to occur. It is preferable that the hardness is ranged between 20 or more and 85 or less.

### (2) Stress when compressed by 300% (kgf/cm<sup>2</sup>) \*\*\* JISK-6301

In the relationship with hardness, the higher the stress when compressed by 300% becomes, the pulsation can be prevented. When the stress when compressed by 300% becomes 22 to 25 kgf/cm<sup>2</sup> under the condition that the hardness is 68 to 65, the pulsation is caused to occur.

## (3) Permanent compression strain (%) \*\*\* JISK-6301 (70 °C × 22 hours)

The permanent compression strain was measured by inserting the gasket into the cylinder of the syringe 1 and leaving it in this condition. For the sealing property to be maintained, it is desirable that the compression set be as small as possible. An appropriate compression set value is in the range of 60% or less.

## (4) Formability

Was evaluated from the fluidity when performing injection molding.

## (5) Mold Appearance

Was evaluated from the flow marks on the mold surface.

## (6) Pulsation

A syringe pump 20 as shown in Fig.2 which is capable of pushing at a constant speed the body to be pushed which had been inserted into the syringe was used. The syringe 1 which had sucked water was engaged to the syringe pump 20. The quantity of injection of water from the syringe by the pushing head 21 of the syringe pump 20 was determined to be 1 ml/hour. The quantity of water injected from the syringe 1 was detected as a water drop of about 1/60ml by a detector 22. The detected results were recorded by a recording device 24 via an amplifier 23 so that the diagram about the signals was obtained as shown in Fig. 2. If the intervals between the signals shown in Fig. 2 are constant, it can be said that the quantity of injection per unit time period is constant and thereby there is no pulsation.

## (7) Oil Bleed

The elution level of the plasticizer was tested. It was evaluated in such a manner that the state of the surface of the gasket at 23 °C for 7 days continued was visually observed.

The mixed components used in the embodiments and comparative examples were as follows:

(a) Hydrogen added derivative of styrene-butadiene block copolymer \*\*\* "KRATON-G1651" manufactured by Shell Chemical (the Brookfield viscosity: 2000cps. 77 °F in 20 wt% toluene solution)

(b) plasticizer \*\*\* "PW380" fluid paraffin manufactured by Idemitsu Kosan (kinetic viscosity at 40 °C: 381.6cst)

(c-1) Polyethylene resin \*\*\* Polyethylene-HD "JX-10" manufactured by Mitsubishi Petrochemical, Co. Ltd. (density : 0.956g/cm<sup>3</sup>, MFR:190 °C, 20g/10min)

(c-2) Polyethylene resin \*\*\* Polyethylene-HD "JX-20" manufactured by Mitsubishi Petrochemical, Co. Ltd. (density : 0.964g/cm<sup>3</sup>, MFR : 190 °C, 5.5g/10min)

(c-3) Polyethylene resin for comparative example \*\*\* Polyethylene-HD "MS-30" manufactured by Mitsubishi Petrochemical, Co. Ltd. (density : 0.918g/cm<sup>3</sup>, MFR : 190 °C, 20g/10min)

(c-4) Polypropylene resin for comparative example \*\*\* "Mitsubishi Polypro BC5C" (MFR : 5g/10 min)

(d) Hydrocarbon-type wax ... Polyethylene wax "A-C Polyethylene, A-C8" manufactured by Allied signal in the United States (dropping point: 116 °C, Brookfield viscosity: 400cps. 140 °C)

## Examples 1 to 10 and Comparative Examples 11 to 12

Phenol antioxidant "Irganox 1010" was added by 0.1 parts by weight as a stabilizer to the mixtures shown in Table 1 with respect to 100 parts of the mixtures. Then, it was fused and kneaded by a two-shaft extruder of L/D = 33 and the cylinder diameter of 45mm at predetermined temperature 220 °C so that TPE pellet was obtained.

The 2mm-thickness sheet to be tested and the gasket to be tested and having the peak diameter of

13.2mm were manufactured by the above-described injection molding in which the pellet described above was used. The results of the various evaluations about the obtained sheets and gaskets are shown in Table 1.

Example 1 to 3, 7, and 8 are gaskets according to Claim 1. They exhibit a high stress under the same hardness, have a small permanent compression strain, and provide a satisfactory rubber elasticity. They exhibit satisfactory characteristics in respect of pulsation and oil bleed. In particular, Example 1 to 3 are gaskets having particular mixture proportions as claimed. They excel in all respects, i.e., in formability, mold appearance, pulsation, and oil bleed.

Examples 4 to 6, 9, and 10 are gaskets according to Claim 3. They excel in all respects, i.e., in formability, mold appearance, pulsation, and oil bleed. In particular, Examples 4 to 6 are gaskets having a particular mixture proportion as claimed in Claim 4, and provide a particularly excellent mold appearance.

Table 1

|                                     |       | Example |    |    |    |    |    |    |    |      |      | Comparative Example |    |
|-------------------------------------|-------|---------|----|----|----|----|----|----|----|------|------|---------------------|----|
|                                     |       | 1       | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9    | 10   | 11                  | 12 |
| Mixture(wt%)                        | a     | 50      | 45 | 50 | 50 | 45 | 50 | 70 | 50 | 50   | 50   | 50                  | 50 |
|                                     | b     | 50      | 55 | 50 | 50 | 55 | 50 | 30 | 50 | 50   | 50   | 50                  | 50 |
|                                     | c - 1 |         | 17 | 13 | 13 | 15 | 13 |    |    |      |      |                     |    |
|                                     | c - 2 | 15      |    |    |    |    |    | 10 | 5  | 60   | 10   |                     |    |
|                                     | c - 3 |         |    |    |    |    |    |    |    |      |      | 40                  |    |
|                                     | c - 4 |         |    |    |    |    |    |    |    |      |      |                     | 20 |
|                                     | d     |         |    |    | 5  | 5  | 10 |    |    |      | 30   |                     |    |
| JIS-A hardness                      |       | 65      | 57 | 55 | 60 | 70 | 65 | 63 | 37 | 98NG | 82   | 69                  | 68 |
| 300% stress(kgf/cm <sup>2</sup> )   |       | 36      | 35 | 31 | 35 | 38 | 37 | 48 | 26 | 93   | 53   | 32                  | 22 |
| Permanent Compression strain (%)    |       | 29      | 26 | 25 | 27 | 31 | 33 | 25 | 23 | —NG  | 68NG | 73NG                | 44 |
| Formability at molding              |       | G       | G  | G  | G  | G  | G  | NG | NG | G    | G    | G                   | G  |
| Mold appearance                     |       | G       | G  | G  | E  | E  | E  | —  | —  | G    | G    | G                   | G  |
| Pulsation                           |       | G       | G  | G  | G  | G  | G  | G  | G  | G    | G    | G                   | NG |
| Oil bleed                           |       | G       | G  | G  | G  | G  | G  | G  | G  | G    | G    | NG                  | G  |
| E : Excellent G : Good NG : No Good |       |         |    |    |    |    |    |    |    |      |      |                     |    |

## Claims

(1) A gasket made of a composite comprising hydrogen-added derivative (component a) of styrene-butadiene block copolymer, plasticizer (component b), and a polyethylene resin having a density of 0.940g/cm<sup>3</sup> or more (component c).

(2) A gasket according to claim 1, wherein said composite is formed by mixing 100 parts by weight of said component a and said component b with 10 to 50 parts by weight of said component c, said 100 parts being the total of said component a by 40 to 60 wt% and said component b by 60 to 40 wt%.

(3) A gasket made of a composite comprising hydrogen-added derivative (component a) of styrene-

butadiene block copolymer, plasticizer (component b), a polyethylene resin having a density of 0.940g/cm<sup>3</sup> or more (component c), and a hydrocarbon-type wax (component d).

(4) A gasket according to claim 3, wherein said composite is formed by mixing 100 parts by weight consisting of said component a and said component b with 10 to 50 parts by weight of said component c, and 2 to 20 parts by weight of said component d, said 100 parts being the total of said component a by 40 to 60 wt% and said component b by 60 to 40 wt%.

(5) A medical device comprising a cylindrical body and a gasket arranged in close contact with the inner surface of said cylindrical body and adapted to slide therein, said gasket being one obtained in accordance with any one of Claims 1 to 4.

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FIG. 1

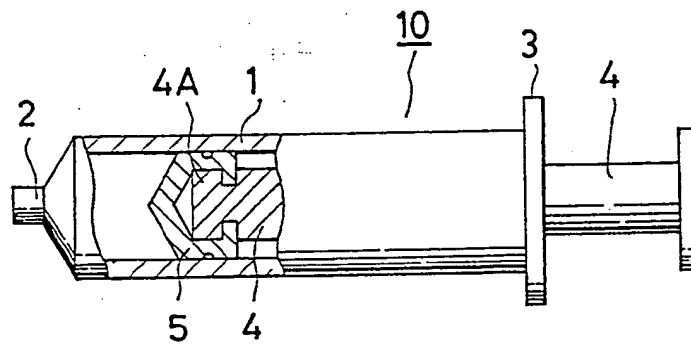


FIG.2(a)

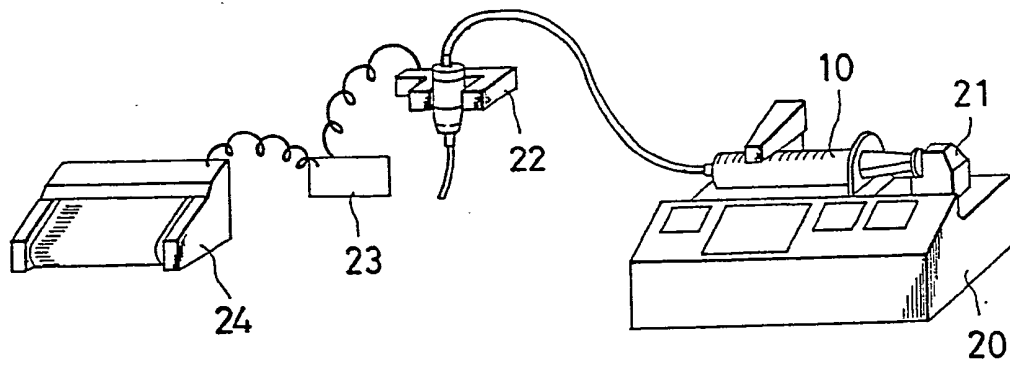
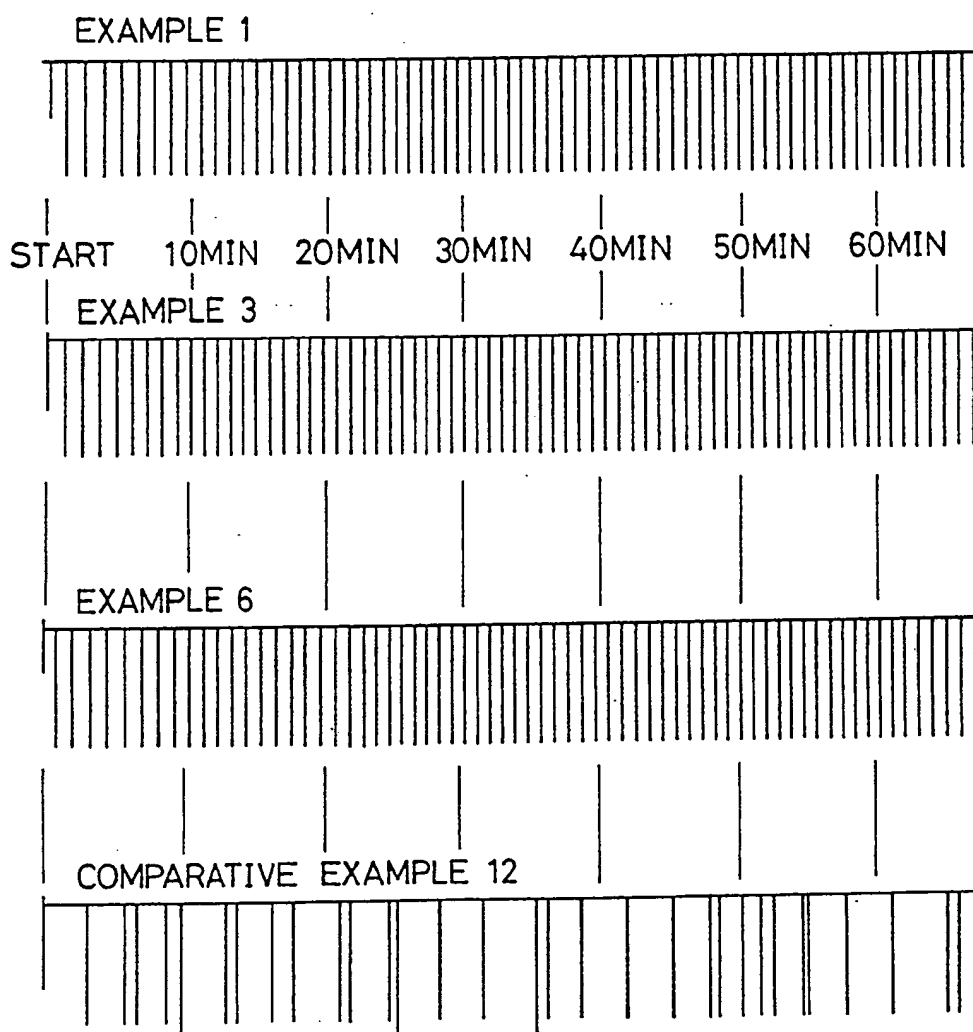


FIG.2(b)



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